

## CHAPTER 9

### Activated Carbon and Membrane Processes for Disinfection By-Product (DBP) and Microbial Control<sup>1</sup>

#### Introduction

It is likely that many utilities will be able to meet current and upcoming drinking water regulations for DBPs by implementing one of the following relatively low-cost options: changing coagulation conditions, changing the point of chlorination, or switching to an alternative disinfectant (Symons et al. 1981). However, some utilities may wish to utilize activated carbon or membranes either because a lower-cost solution is not practical or because they wish to take advantage of the unique properties of activated carbon or membrane processes. Activated carbon and membrane processes are considered higher-price options (compared to enhanced coagulation) for DBP precursor removal and would most likely require major plant construction, hence they are considered together in this chapter. For point-of-use or point-of-entry discussions, the reader is referred to Chapter 11, “Controlling Disinfection By-Products (DBPs) and Microbial Contaminants in Small Public Water Systems (PWSs).”

For both GAC and membrane processes, it is more economical to remove the DBP precursor material than the formed DBPs. DBP precursors, as a whole, are more readily adsorbed onto activated carbon than DBPs (Symons et al. 1981). Precursor materials have larger molecular sizes than DBPs; therefore, it is easier for membranes to reject precursor material. Also, both activated carbon and membranes have problems handling chlorinated water. Activated carbon quickly reduces free chlorine. This lowers the capacity of the carbon, makes the carbon more brittle, and increases the amount of dioxins formed upon regeneration (Lykins et al. 1988b). Also, because activated carbon reduces the disinfectant, postfilter chlorination will be needed, which will form additional DBPs from the precursor material that was not adsorbed onto the column. Free chlorine attacks membrane material through oxidation pathways, and failure quickly occurs for many of these chlorine-sensitive thin-film membranes. Thin-film membranes are commonly used today because they have better flux and biodegradation characteristics than chlorine-resistant membranes.

Activated carbon is commonly applied as powdered activated carbon (PAC) or in granular activated carbon (GAC) form. PAC is often applied at, or before, the coagulation/flocculation step. The powdered carbon adsorbs contaminants and natural organic matter (NOM) until it is removed downstream in the sedimentation and filtration processes. Unless specific changes are made to the water treatment train (floc blanket clarifier or membranes), the typical adsorption residence time is too short to remove a significant amount of the NOM (DBP precursors), which generally adsorb slowly as compared to synthetic organic chemicals (SOCs). With regard to prechlorinated waters, the PAC adsorption capacities for DBPs are too low for economical removal (Symons et al. 1981). Therefore, PAC is most often used for SOC or taste and odor control.

GAC is utilized in a filter mode. It can be used as part of a multi-media filter to remove particulates (filter adsorber) or as a postfilter to remove specific contaminants (postfilter adsorber). Filter adsorbers are operated as typical inert-media filters. They are backwashed periodically to alleviate head loss, and the carbon is regenerated very infrequently, if at all. When used in postfilter mode, the bed is rarely backwashed, and the GAC is regenerated as often as needed to control for the contaminant(s) of interest.

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Activated carbon has no specific ability to remove microbial pathogens unless it is used as GAC in a filter adsorber application, where it removes pathogens by the same mechanisms as any other filter media. GAC, due to its typically larger size, does not remove particulates/pathogens to any greater degree than other filter media types, so its use is never recommended if particulate/pathogen removal is the only goal. Therefore, this chapter will only cover activated carbon processes for DBP control.

Certain types of membranes can be very effective for controlling DBPs, while others are specifically designed to remove particulates/pathogens. Reverse osmosis (RO) membranes are very tight membranes that have molecular-weight cutoffs (MWCOs) below 200 daltons. They are typically used to remove salts from seawater and brackish waters. Due to their tight membrane structure, they are operated at very high pressures (10 to 100 bar).

Nanofiltration (NF) membranes are not as tight as RO membranes. The MWCOs for NF membranes are generally considered to range between 200 and 1,000 daltons. They are designed to remove divalent cations, hence they are often referred to as softening membranes, although they have been found to remove a large percentage of DBP precursors. Because they are not as tight as RO membranes, they can be operated at lower pressures (typically 5 to 9 bar) while achieving fluxes that are the same, or greater, than RO membranes. These lower pressures make NF membranes less expensive than RO membranes for a given design flow. Research at the U.S. Environmental Protection Agency (EPA) Office of Research and Development (ORD) has therefore concentrated on NF membranes.

Ultrafiltration (UF) and microfiltration (MF) membranes are typically used only for particulate/pathogen removal. UF membranes have MWCOs that range from 1,000 to 500,000 daltons. While some of the UF membranes that have MWCOs near 1,000 daltons may remove significant amounts of DBP precursor material, the MWCO ranges are arbitrarily set, and therefore, the membrane could be considered a loose NF membrane. MF membranes have an order-of-magnitude larger pore sizes than UF membranes. Typically, MF pores sizes are designated in micrometers and normally range from 0.05 to 5  $\mu\text{m}$ . A rough rule of thumb is that UF membranes can reject viruses, while MF membranes cannot.

This chapter provides a comprehensive review of activated carbon and membrane research for the control of DBPs and pathogens. Much of the work was conducted, or funded, by ORD. Outputs include: peer-reviewed papers, proceedings papers, EPA reports, Master's theses, and Ph.D. dissertations. It also includes other papers that were written under non-ORD projects. Some of these were co-authored by ORD researchers, but many were not. Although the intent is to highlight ORD research, non-ORD projects are included to make the discussion complete.

This work is a follow-up to the EPA work published by Symons et al. (1981). For other recent comprehensive scientific discussions of GAC and membrane technologies, the reader is referred to Jacangelo (1999), Snoeyink et al. (1999), Snoeyink and Summers (1999), and Taylor and Wiesner (1999). Also, the Information Collection Rule (ICR) treatment studies have been recently compiled. The EPA required water utilities of a certain size and water quality to complete GAC or membrane studies so as to create a national data base for advanced DBP removal technologies. The ICR treatment studies were conducted through the auspices of the Office of Ground Water and Drinking Water with very limited ORD involvement.

## **Activated Carbon**

### ***Filter Adsorbers vs. Postfilter Adsorbers***

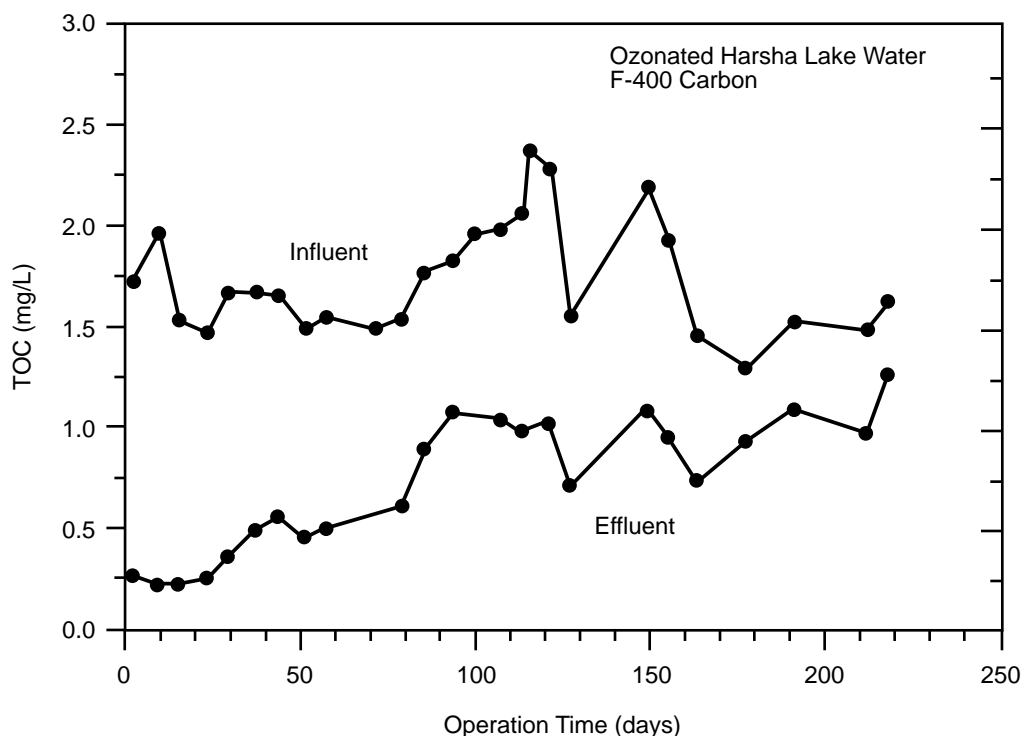
As mentioned previously, the removal of NOM and DBP precursors by PAC is not very efficient (Symons et al. 1981). Therefore, the following discussion will only pertain to GAC filtration technologies. The major limitation for filter adsorbers is their depth. The Ten-State Standards require sand depths of at

least 4 feet. Therefore, this leaves a limited depth of GAC that can be placed above the sand. The lack of depth, or empty bed contact time (EBCT), is crucial for waters that contain moderate- to poor-adsorbing NOM. Early breakthrough would require frequent replacement or regeneration of the carbon. Hartman et al. (1991) determined that filter adsorbers were not cost effective for NOM control. However, due to GAC's ability to maintain a biological community that would remove DBP precursors, systems that need only limited DBP precursor removal may find filter adsorbers to be practical. Wiesner et al. (1987) concluded that filter adsorbers are generally more cost effective than postfilter adsorbers if the desired total organic carbon (TOC) (precursor) removal is less than 55 percent. Under more unique conditions, Wiesner et al. (1987) found that filter adsorbers are cost effective for removals up to 75 percent. Because limited removals can generally be obtained by other means, ORD research has concentrated on postfilter adsorbers which can be highly effective for controlling disinfection by-products under a wide range of conditions.

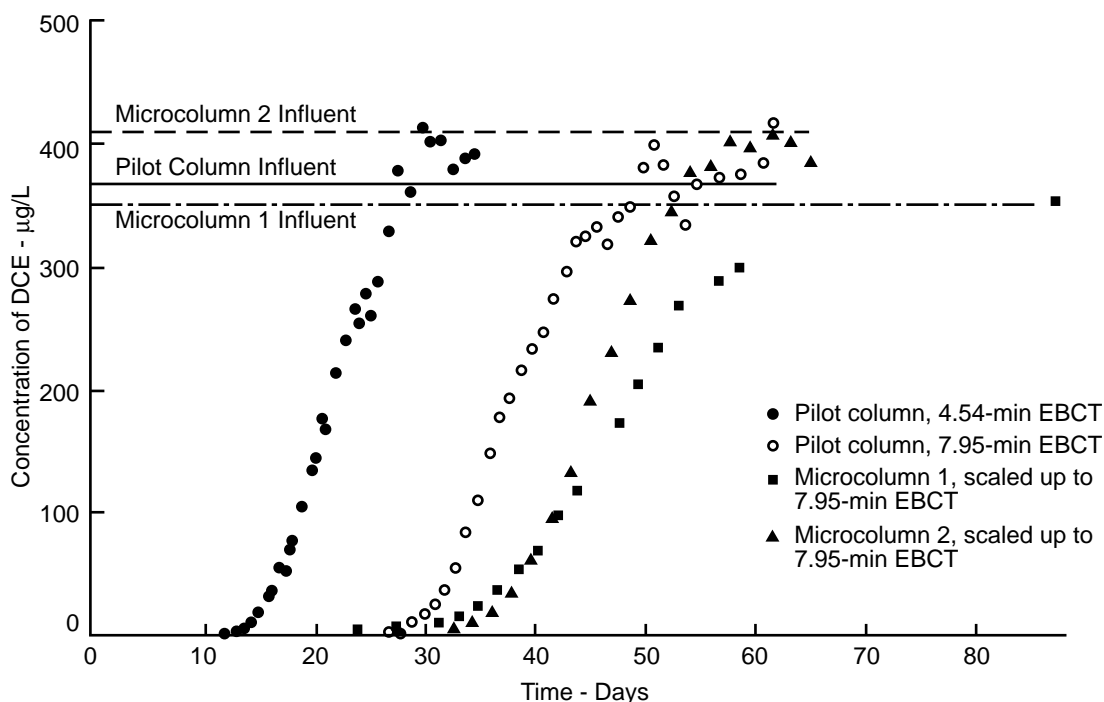
### ***Breakthrough Profiles***

Figure 9-1 contains a typical NOM, as TOC, breakthrough profile for a postfilter GAC column (Miltner et al. 1996). There is immediate TOC breakthrough because a certain portion of the TOC is nonadsorbable. The effluent TOC concentration then slowly increases toward the influent concentration. The breakthrough profile eventually plateaus as the biodegradable or slowly adsorbing fractions are removed.

These results are different than for SOC's that generally show complete removal for a period of time, followed by a sharp "S"-shaped breakthrough to the influent level as shown in Figure 9-2 (Speth and Miltner 1989). Singer (1994) found that three-to six-month run times between regenerations were most common for NOM removal.

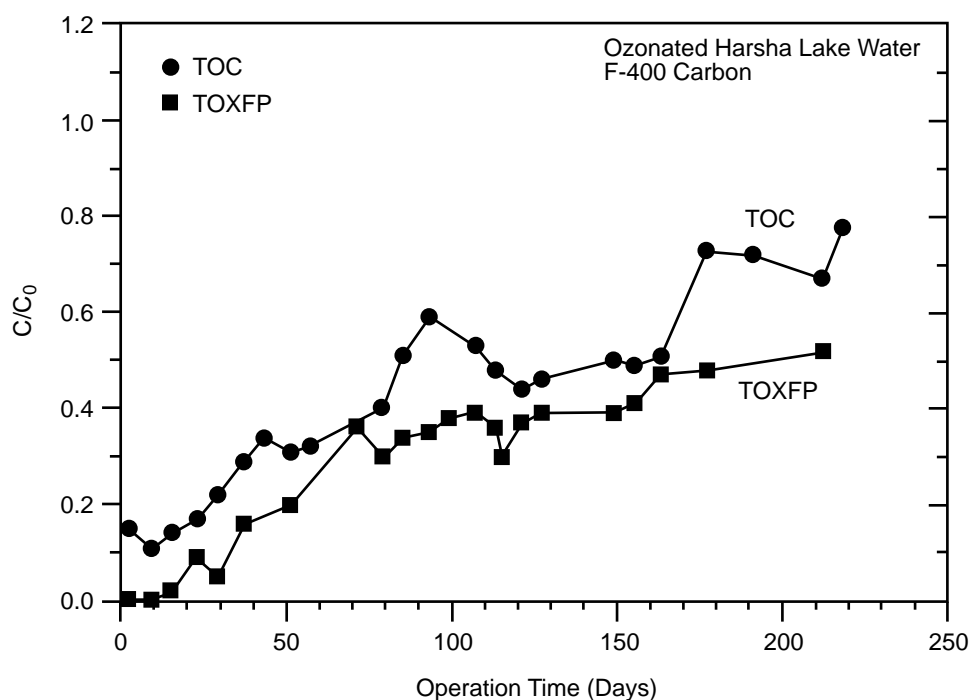


**Figure 9-1. TOC breakthrough profile for F-400 carbon treating ozonated Harsha Lake water (Miltner et al. 1996).**



**Figure 9-2. Breakthrough profile for cis-dichloroethene (Speth and Miltner 1989).**

The breakthrough of certain DBP precursors mimics that of TOC breakthrough (Lykins et al. 1988a; Symons et al. 1981; Summers et al. 1995; Miltner et al. 1996). Figure 9-3 shows breakthrough profiles for TOC and total organic halide formation potential (TOXFP) (Miltner et al. 1996). As can be seen, TOC is an accurate predictor of TOXFP.



**Figure 9-3. Breakthrough profiles for TOC and TOXFP (Miltner et al. 1996).**

Even though DBP formation potential (DBFP) breakthrough can be predicted by TOC breakthrough, a GAC column's performance for controlling DBPs is not always straightforward. The GAC adsorption performance is predicated on an interwoven matrix of system design, water quality, and chlorination conditions.

### ***GAC Adsorption Performance***

There are many factors that affect GAC adsorption performance. Assuming instantaneous kinetics, an equation to calculate the time to breakthrough in days is:

$$\text{Time to breakthrough (days)} = (K C_o^{1/n} Wt) / (Q C_o) \quad (9-1)$$

where  $K$  and  $1/n$  are the Freundlich constants in  $\mu\text{g/g (L}/\mu\text{g)}^{1/n}$ ,  $C_o$  is the influent concentration in  $\mu\text{g/L}$ ,  $Wt$  is the weight of carbon in g, and  $Q$  is the volumetric flow rate in L/day.

Clark et al. (1986) and Clark (1987) developed the logistic function which describes the TOC effluent concentration in terms of time, initial concentration, EBCT, and adsorption capacity as represented by the Freundlich equation.

$$\text{TOC}_f = ([\text{TOC}_o]^{n-1}) / (1 + A e^{-rt})^{1/n-1} \quad (9-2)$$

where  $A$  and  $r$  are fitting parameters,  $\text{TOC}_f$  is the effluent TOC concentration,  $\text{TOC}_o$  is the influent TOC concentration,  $t$  is time, and  $n$  is the Freundlich parameter. The fitting parameters  $A$  and  $r$  were further related to EBCT. The exact equations were determined by fitting the following equations to breakthrough profiles from GAC columns at Jefferson Parish (Clark 1987)

$$A = 0.757(\text{EBCT})^{1.35} \quad (9-3)$$

$$r = 0.0743(\text{EBCT})^{-0.429} \quad (9-4)$$

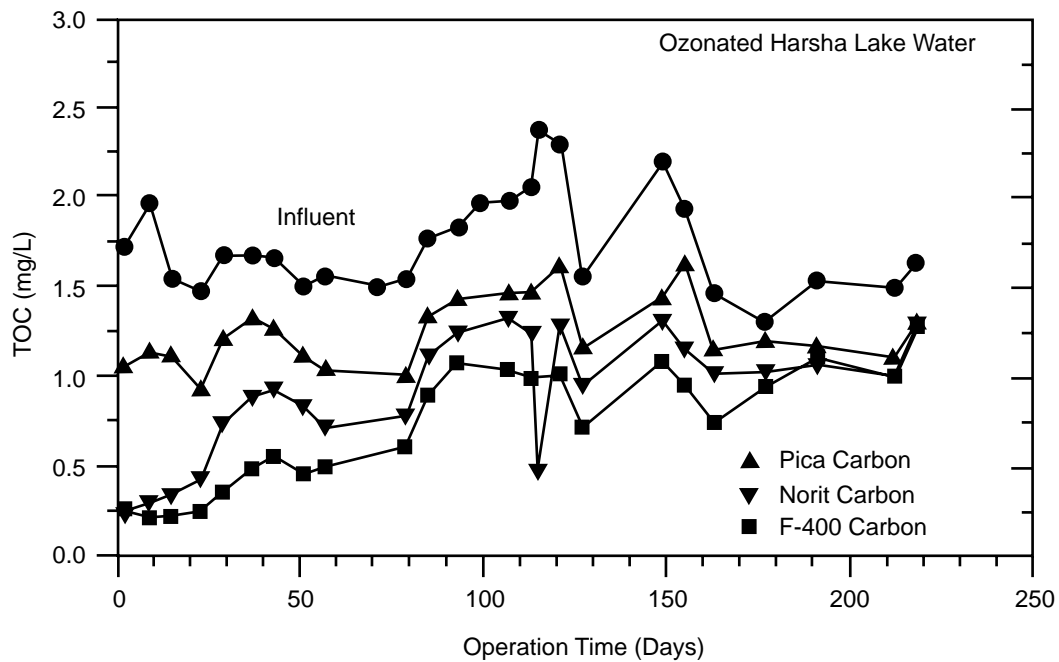
where EBCT is the empty bed contact time (volume of the bed divided by the volumetric flow rate).

The preceding equations demonstrate the importance of TOC adsorbability, initial concentration, and EBCT for a given carbon. Many other models have been developed for GAC adsorption; however, they have limited applicability to DBP precursor adsorption because of the undeterminable heterogeneity of the natural organics in the influent water. Luft (1984), Crittenden et al. (1987b), Speth (1986), Warta et al. (1995), and Hong (1985) have worked with limited success in developing and applying hypothetical components for predicting TOC adsorption.

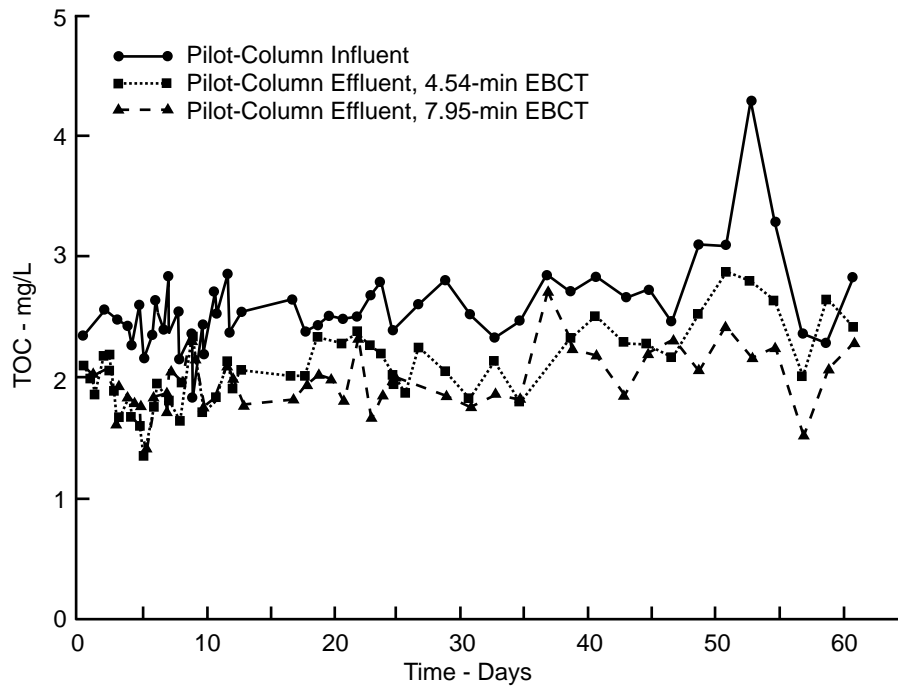
### ***Adsorbability***

Different carbons will adsorb DBP precursors to varying degrees. Figure 9-4 shows the breakthrough profiles for three different activated carbons that treated ozonated Harsha Lake Water (Miltner et al. 1996). Wang et al. (1995) found that trihalomethane formation potential (THMFP) removals ranged from 27 to 40 percent, while TOXFP removals ranged from 31 to 52 percent depending on what type of carbon was used.

The NOM and DBP precursors of different waters will adsorb to different extents. Figure 9-5 shows an atypical TOC breakthrough profile for a ground water from Fairfield, OH, using F-400 carbon (Speth and Miltner 1989). In this case, approximately 80 percent of the NOM in the Fairfield water was nonadsorbable. These results can be compared to those in Figure 9-1 for Harsha Lake water. The NOM in the Harsha Lake water was adsorbed to a much greater extent.



**Figure 9-4. TOC breakthrough profiles for different activated carbons treating ozonated Harsha Lake water (Miltner et al. 1996).**



**Figure 9-5. TOC Breakthrough profile for ground water from Fairfield, OH (Speth and Miltner 1989).**

Generally, smaller NOM molecules adsorb more strongly than larger ones because pore blockage of large molecules can limit the accessibility to adsorption sites. Also, the greater the hydrophobicity of the NOM, the greater the adsorption. Aromatic compounds are generally more strongly adsorbed than nonaromatic compounds. Therefore, terrestrial-derived organic compounds which tend to have greater aromatic character are expected to adsorb to a greater extent than aquatic-derived ones. Proteinaceous compounds are also known to be strongly adsorbed.

The Polanyi potential model can predict adsorption capacities based on the following equation (Speth 1986; Speth and Adams 1991). The Polanyi theory assumes there is a fixed volume close to the adsorption surface where adsorption occurs. The volume is defined by equipotential surfaces which describe the amount of work needed to move any molecule from the bulk solution to the adsorption space. A final form of this development is:

$$K = \rho W \exp((- \rho B R T \ln (C_s)) / M_w) \quad (9-5)$$

where K is the Freundlich parameter,  $\rho$  is the compound density, W and B are fitting constants, R is the ideal gas constant, T is temperature,  $C_s$  is the compound's water solubility, and MW is its molecular weight. The Freundlich K can be used to judge the relative strength of adsorption for a specific compound. As can be seen, if a water has constituents with low solubilities, the capacity of the carbon for that constituent will be high. Also, a lower temperature and higher MW will result in greater adsorption (assuming no pore blockage). Crittenden et al. (1999) has further evaluated adsorption correlations.

Isotherm data for specific contaminants are valuable because kinetic models have been developed to predict full-scale results from isotherm data. Speth and Miltner (1990, 1998) contain isotherm data for numerous DBPs. However, kinetic models are not useful for complex mixtures such as NOM or DBP precursors. Although attempts have been made (Luft 1984; Crittenden et al. 1987b; Speth 1986; Warta et al. 1995; Hong 1985), it is very difficult to predict NOM adsorption.

The logistic function (Equation 9-2) may be the best way to predict GAC performance for the adsorption of NOM. The logistic function's adsorption parameters were determined by fitting the breakthrough profiles from Jefferson Parrish, LA. These NOM breakthrough profiles had moderate adsorbability as compared to other available data.

### ***Initial Concentration***

Initial concentration is a function of the water's source, although it can be affected by pretreatment processes. Different pretreatments will also affect the adsorbability and biodegradability of the NOM. As mentioned earlier, chlorination has a detrimental effect on the control of DBPs primarily due to the lower adsorption capacity of GAC for formed DBPs and detrimental surface reactions with the activated carbon. Semmens et al. (1986b) showed that alum coagulation resulted in improved GAC run times for TOC and THM precursor removal because of reduced initial concentration and the removal of poorly adsorbed high-molecular-weight organics. Hooper et al. (1996) found that enhanced coagulation reduced the concentration of the NOM, but also increased its adsorbability due to the reduced pH imparted from the increased alum dose.

Ozonation makes the NOM more polar, and hence less adsorbable, but it also increases its biodegradability (Sontheimer and Hubele 1987). Therefore, for short beds that are regenerated frequently, preozonation would not be helpful, whereas for longer beds that are infrequently regenerated, preozonation would be a benefit. The reader is referred to other chapters which discuss preozonation's effect on subsequent chlorination reactions (Chapter 5) and preozonation's effect on biodegradation (Chapter 6).

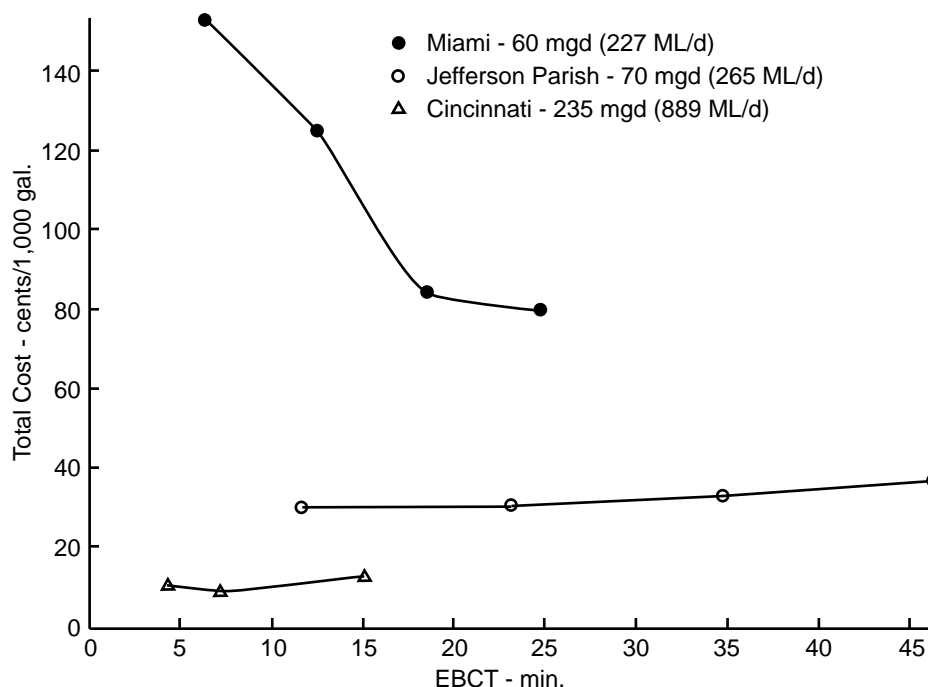
Benz et al. (1992) showed that anion exchange pretreatment can significantly improve the performance of GAC columns. The anion exchange columns extended the GAC performance by a factor of two to three for NOM and DBP precursors. The resin removed the hydrophilic weakly adsorbing NOM that was not amenable to GAC treatment.

Finally, inorganic precipitation can foul GAC. Coagulants can result in an oversaturation of calcium carbonate or iron hydroxides. Also, if air is introduced into an anaerobic ground water, iron and manganese precipitation can coat the carbon, reducing its capacity and slowing film transfer kinetics (Speth 1991).

## ***EBCT***

As can be seen in Equation 9-1, EBCT is an important parameter for adsorption performance in GAC columns. The greater the EBCT, the longer the column will remain operational. Figure 9-2 shows the cis-dichloroethene breakthrough profiles for two different EBCTs. As can be seen, the breakthrough profile for the longer EBCT occurs later than the shorter EBCT, as expected. However, doubling the EBCT generally does not necessarily double the run-time length. Summers et al. (1995) showed that columns with EBCTs of 10 and 20 minutes had similar carbon use rates for removing NOM. This suggested that utilities should attempt to minimize the EBCT to reduce capital costs. Wiesner et al. (1987) found that 6 to 12 minutes of EBCT was optimal for TOC removal.

Lykins et al. (1988a) showed that the most cost-effective EBCT will depend on the source water. Figure 9-6 shows the plot of costs versus EBCT. The costs for Jefferson Parish and Cincinnati water did not vary greatly with EBCT, whereas Miami water shows a clear advantage of longer EBCTs. Because of the tradeoff between cost of replacement/regeneration and the increased capital cost of the larger columns, EBCTs typically range somewhere between 10 and 20 minutes. As with the other design factors, the total cost will be a function of how the column effluents are blended together. This issue will be discussed later in this chapter.



**Figure 9-6. Costs versus EBCT for three waters (Lykins et al. 1988a).**



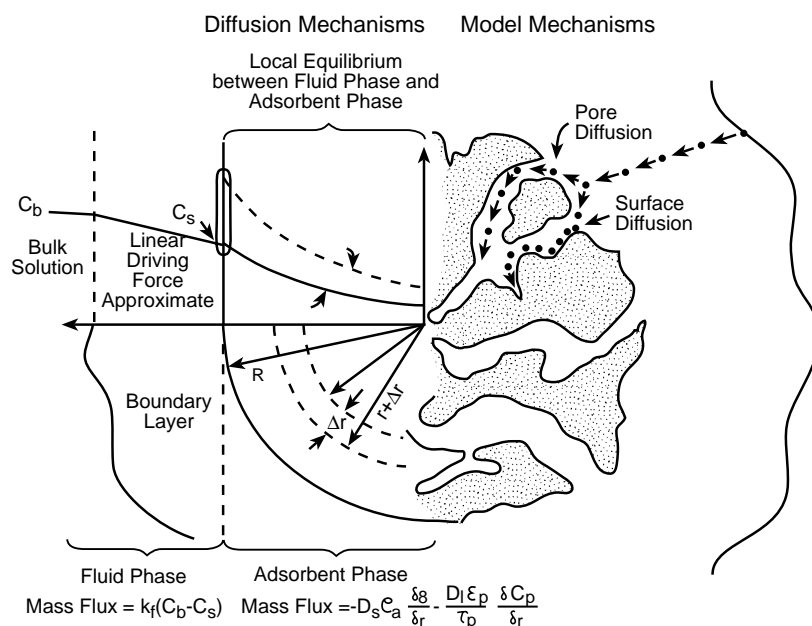


Figure 9-7. Adsorption kinetics (Crittenden et al. 1987c).

### Adsorption Kinetics

Adsorption kinetics also influence the shape of the adsorption profile. Mechanisms of adsorption kinetics include film diffusion, pore diffusion, and surface diffusion. Figure 9-7 shows the adsorption kinetics around and within a carbon particle (Crittenden et al. 1987c). Kinetic models must account for external (film transfer) and internal (pore and surface diffusion) effects. Slow kinetics will result in a flat breakthrough profile, whereas fast kinetics will result in a steep profile. If the kinetics of adsorption are instantaneous, the breakthrough profile for a single compound will be a step function as shown in Figure 9-8 (Speth 1990). For NOM breakthrough, the breakthrough profile will be flattened even if the kinetics of adsorption are instantaneous. This is because NOM is made up of countless different types of compounds that will breakthrough at different times. In this case, the breakthrough profile will be a series of infinitely small steps.

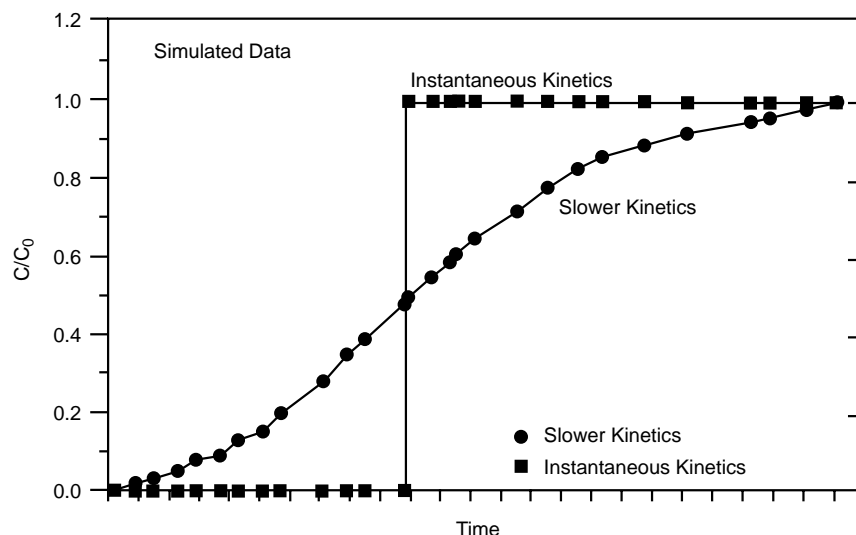


Figure 9-8. SOC Breakthrough profiles assuming slow and instantaneous kinetics.

The size of GAC particles used in full-scale columns varies within standard ranges. Postfilter carbon is typically 12 × 40 mesh (1.68 by 0.42 mm), although other sizes are also on the market. These ranges will not, however, produce markedly different adsorption results in a postfilter adsorber. The choice of carbon size is often determined by the smallest size that does not create head loss problems because smaller carbon particles will have faster kinetics, resulting in more efficient bed adsorption. For postfilter adsorbers, this is typically 12 × 40-mesh carbon.

Crittenden et al. (1986, 1987a) developed the Rapid Small Scale Column Test (RSSCT) to help predict full-scale adsorption data. The RSSCT uses smaller particle sizes to obtain full-scale results in a fraction of the time needed to run a pilot column. For example, a RSSCT can be completed in 1 month and be representative of a year-long full-scale study. Therefore, seasonal studies can be conducted without having to account for major changes in influent water quality. Scale-up approaches were developed for a number of diffusivity assumptions. Summers et al. (1995) found that the proportional diffusivity approach developed by Crittenden et al. (1987a) was the most appropriate for TOC breakthrough profiles. However, although useful for planning, the RSSCT is only for pilot-scale design and does not hold practicality for full-scale systems (Speth and Miltner 1989; Speth et al. 1989).

## pH

NOM is predominantly negatively charged. Therefore, decreasing the pH renders the predominantly negatively charged organic molecule more neutral. A neutral compound is inherently less soluble in water than a charged molecule and, therefore, more adsorbable. Also, at low pHs, NOM is more coiled due to a less negative-charge repulsion. This may allow for greater access to GAC pores. Semmens et al. (1986a) showed that a lower pH will result in better adsorption. Figure 9-9 shows TTHMFP breakthrough profiles for the same water at different pHs. The lower pH system had a longer bed life. Hooper et al. (1996) also concluded that lower pHs improved NOM/precursor adsorbability.

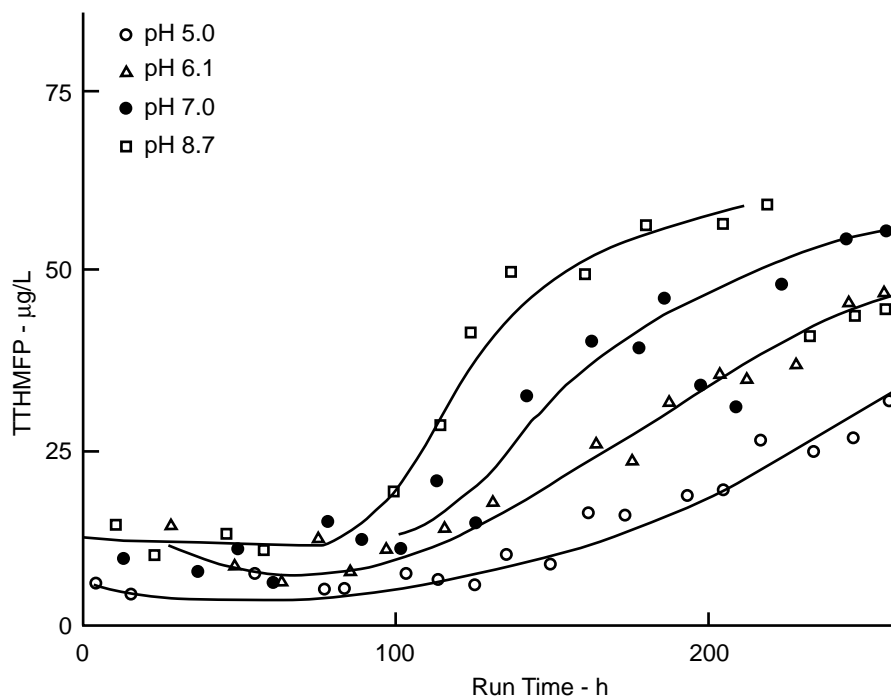
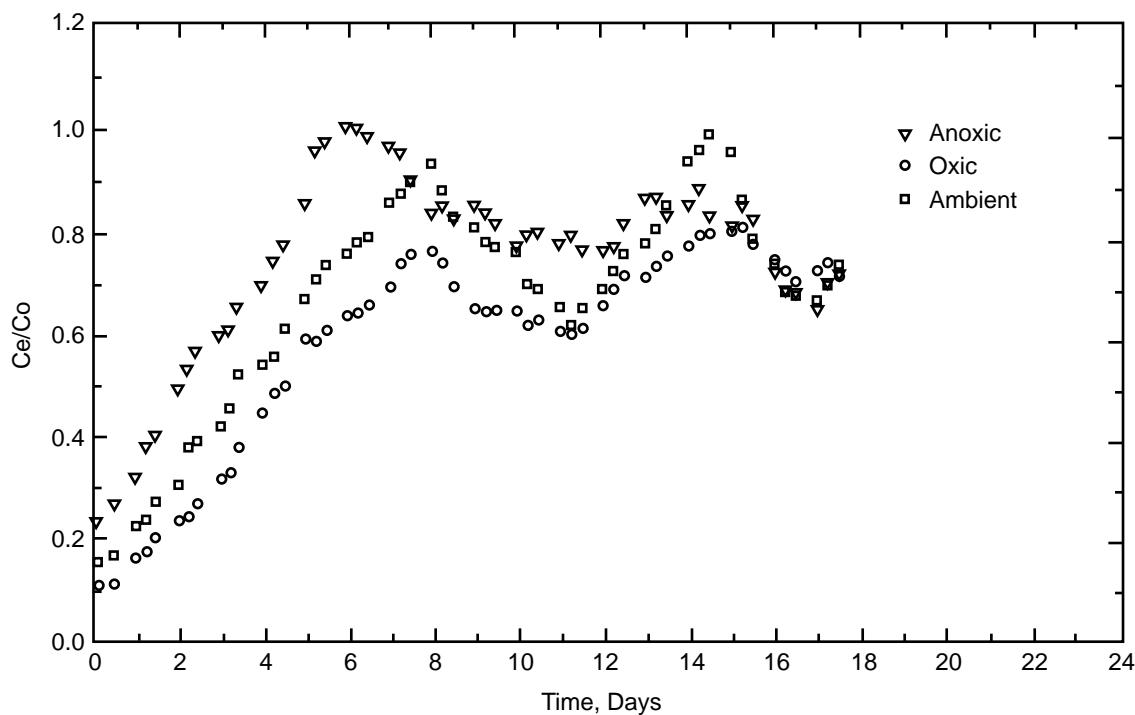


Figure 9-9. Effect of pH on TTHMFP adsorption (Semmens et al. 1986a).

## Biogrowth and Dissolved Oxygen

As mentioned previously, biogrowth can improve GAC bed performance for removing DBP precursors. Therefore, introducing oxygen to encourage biogrowth can result in greater biological removal of DBP precursors. Dissolved oxygen also has shown to increase the adsorption of NOM due to their polymerization onto the carbon surface (Warta 1993; Warta et al. 1995). Figure 9-10 shows an example of greater NOM adsorption at high dissolved oxygen levels (Warta et al. 1995). This utility that is drawing anoxic water might consider aerating the water prior to adsorption for maximum NOM removal, although secondary effects such as iron precipitation would have to be taken into account. This increased NOM removal lowers the performance of a column that is treating a specific organic compound that does not polymerize on the GAC surface because the polymerizing NOM competes against the organic compound more effectively for adsorption sites (Vidic et al. 1992; Sorial et al. 1994a; Sorial et al. 1994b; Cerminara et al. 1995). Interestingly, although oxidic polymerization significantly increases the removal of dissolved oxygen content (DOC), Warta (1993) showed that oxidic polymerization only slightly increases the removal of THMFP and TOXFP. Apparently, the fractions of NOM that polymerize on the carbon surface are not precursor material. Warta (1993) did show that air-saturated oxygen levels can significantly increase the removal of THMFP and TOXFP over anoxic and super-saturated oxygen systems. This is presumably due to microbiological processes.

Biological growth occurs in every GAC column that treats drinking water. This is even true for prechlorinated waters because disinfectants are reduced in the top few centimeters of a carbon bed. There are advantages to maintaining biological activity in GAC beds. As mentioned, bioactivity can improve the DBP-precursor-removal performance of GAC columns (Miltner et al. 1994; Miltner et al. 1996; Wang et al. 1995; Warta 1993). Because GAC columns are biologically active, there is typically an increase in the concentration of microbes in the effluent as compared to the influent (Symons et al. 1981). Cold-water systems were found to be the exception, most likely due to the



**Figure 9-10. TOC breakthrough profiles under anoxic, oxic, and ambient conditions (Warta 1993).**

inhibitory effect of low temperatures on microbial growth. Symons et al. (1981) found that adequate post-GAC disinfection produced waters of acceptable quality. Camper et al. (1987) found that GAC columns released disinfection-protected particles that were highly populated with heterotrophic plate counts (HPCs) and coliform bacteria. Camper et al. (1987) concluded that increased bed depth, higher applied-water turbidity, and increased filtration rate exacerbated the bacteria-laden particle problem.

In cases where there is no postfilter disinfectant, such as in-home treatment devices, biological activity is definitely not desired. Silver impregnation has been used to reduce biogrowth, however, Reasoner et al. (1987) found that point-of-use GAC devices that contained silver had concentrations of heterotrophic bacteria as high as units that did not contain silver. Also, it is expected that fouling will further reduce the biocidal properties of the silver. Aside from using preoxidants and adjusting the rate of replacement, or regeneration, a water utility has little control over biodegradation other than to increase it. As previously mentioned, oxidants such as ozone can increase the biodegradability of the NOM in the water. A carbon column that is replaced, or regenerated, frequently (every 1 to 2 months) will not show significant biodegradation. Therefore, it is generally beneficial to lengthen the run time of each column, such as by blending the effluents of multiple columns. The reader is referred to Chapter 6, “Alternative Disinfectants,” for a more in-depth discussion of biological filtration.

### ***Other Effects***

Backwashing is sometimes required to remove particulates from GAC filters. Hong (1985) showed that backwashing had little impact on the removal of TOC and THM precursors for five natural waters.

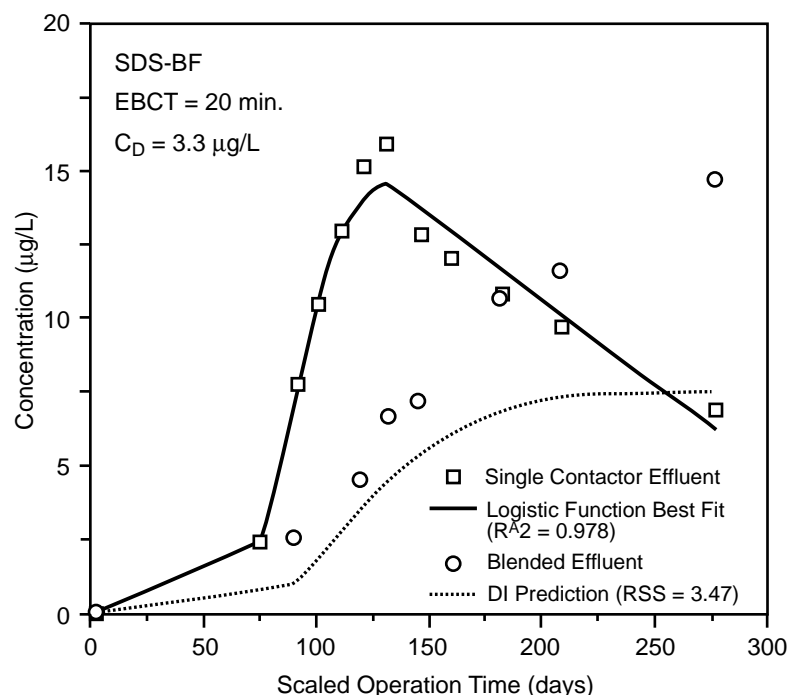
Because adsorption is an exothermic reaction, greater adsorption will occur at lower temperatures. This can be seen in Equation 9-5. Therefore, utilities find better TOC removal in the winter months. This is only one example showing that seasonal effects will change the adsorption characteristics of DBP precursors. Another seasonal change includes changes in the NOM characteristics because of algal and microbial production during the summer months. Neither temperature nor NOM quality is an adjustable parameter for a water utility.

### ***Bromide Issues***

The prediction of brominated DBP breakthrough from GAC columns is more complicated than for certain chlorinated DBPs. Brominated THMs are often found to be elevated in GAC effluent water (Symons et al. 1981). The formation of brominated DBPs is a function of the bromide-to-NOM ratio and the bromide-to-chlorine ratio (Summers et al. 1993). (Refer to Chapter 2 for a speciation discussion.) Because GAC columns remove NOM but do not remove bromide, the bromide-to-NOM ratio in the column effluent will be constantly changing. Early in the column run, the bromide-to-NOM concentration will be very high. This will favor the formation of brominated DBPs over chlorinated DBPs. Eventually, the NOM concentration in the effluent will increase, resulting in higher chlorinated DBPs. Because of this effect, the precursors to the chlorinated DBPs will appear to be removed better than if no bromide was present. Also, and more importantly, the concentration of brominated DBPs may increase quickly and then later drop. Figure 9-11 shows the breakthrough of SDS-bromoform (USEPA 1999). The effluent peaks were much higher than the influent SDS-bromoform concentration due to excess bromide to TOC in the effluent. Eventually, the remaining TOC breaks through, and the SDS-bromoform returns to influent levels.

### ***Blending***

Greater GAC capacity can be realized if columns are run in parallel or in series. If the start times of the columns are staggered, the first column can be run beyond the maximum total effluent concentration because its effluent is being blended with columns in the start of their breakthrough profiles. Hence, the



**Figure 9-11. SDS-Bromofrom breakthrough with model predictions (USEPA 1999).**

total blended effluent still remains below the design effluent concentration. Roberts and Summers (1982) developed a strategy to calculate the benefit of a parallel approach.

For columns in series, the first column can be run to exhaustion, while the TOC mass transfer zone, or breakthrough profile, is contained in the latter columns. When the first column reaches its maximum operational capacity, it can be taken out of series, and the column can be restarted as the last column with fresh GAC. This approach may be best for SOC removal when the breakthrough profile is relatively sharp. The results of Summers et al. (1995) seem to suggest that the NOM breakthrough profiles are too broad for series operation.

## Membranes

### *Membrane Type*

Membranes remove organic compounds, inorganic compounds, and particulates by creating a barrier through which water is preferentially passed. The rejection can be physical or electrochemical. There are many types of membranes that are manufactured, with each having different stability, flux, and rejection characteristics. The type of membranes studied at the EPA were strictly pressure-driven processes such as RO, NF, UF, and MF because these types of membranes have the most applicability to drinking water systems. Membranes with other driving forces such as electric potential and temperature have not been studied. As stated earlier, both RO and NF membranes are fully capable of rejecting DBP precursors; however, higher fluxes from the NF systems make them generally more economical than RO membranes. Although there may be instances where RO membranes have site-specific advantages over NF membranes (i.e., brackish and sea waters), the following discussion will concentrate on NF. The EPA has conducted the majority of its membrane research with NF membranes because of the need to determine the potential for lowering the current maximum DBP levels in drinking water in a cost-effective manner.

Although a NF membrane is inherently a barrier process, membrane manufacturers are reluctant to claim log-removal credit for pathogens due to the potential of glue-line failure. Also, many plants blend pretreated feed waters with the membrane-treated waters to create a less corrosive product water. This practice results in limiting the microbial removal for NF and RO membranes. Therefore, although particulate/microbial removals may be given for NF membranes, this should not be construed as a basis for log removal credit.

Both UF and MF systems are capable of excellent particulate/pathogen removal; however, their DBP removal performance is more consistent with that seen for conventional treatment (10 to 50 percent). Due to the applicability and the economies of scale that favor using UF and MF for small systems, refer to Chapter 11, “Controlling Disinfection By-Products (DBPs) and Microbial Contaminants in Small Public Water Systems (PWSs),” for an additional discussion of these technologies.

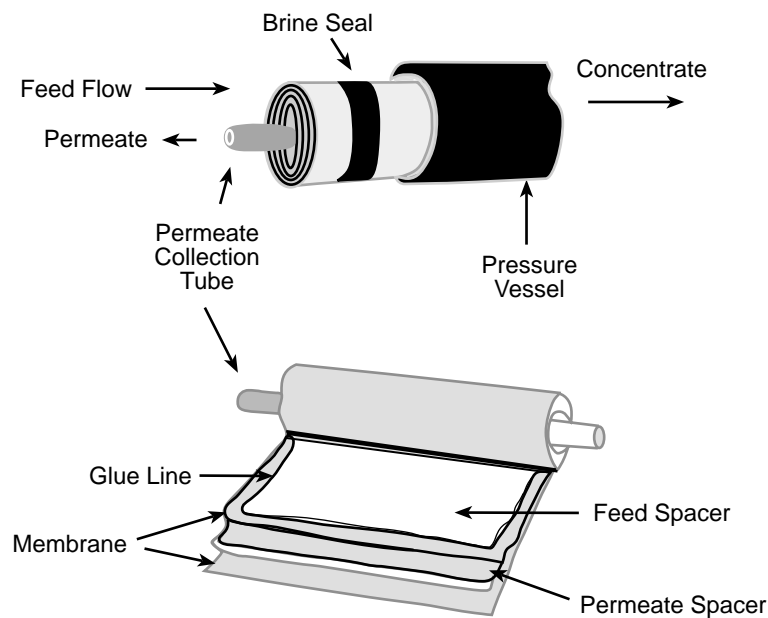
Membranes are made of many materials. Common membrane materials are polysulfone, cellulose acetate, polycarbonate, polypropylene, polytetrafluoroethylene, and polyacrylonitrile. These materials can be classified as hydrophobic or hydrophilic. Membranes made of polyamide, polysulfone, polypropylene, or polytetrafluoroethylene are generally considered hydrophobic membranes. Membranes made of cellulose acetate or polyacrylonitrile are generally considered hydrophilic. Hydrophilic membranes do not foul as fast as hydrophobic membranes (Lainé 1989; Bonner and O’Melia 1991; Eykamp 1978). However, the anti-fouling behavior of hydrophilic membranes is offset by their limitations with regard to pH, chemical, and temperature resistance. This is important for drinking water applications because membrane cleaning is often completed at extreme pHs.

Membranes can be of homogeneous, asymmetric, or composite construction. Composite membranes are most popular due to the thin separation layer that allows for maximization of water flux. The Desal-5, Film-Tec NF-70, Film-Tec NF90, and Fluid Systems’ TFCS membranes are of composite thin film design. The film layers on these membranes are of polyamide construction. Reiss et al. (1999a) found that for NF membranes of comparable productivity, NOM rejection was greater for the polyamide versus cellulose acetate membranes. Membranes typically carry a charge. Polyamide, polysulfone, cellulose acetate, and ceramic membranes carry a negative charge (Lahoussine-Turcaud et al. 1990). The charge of a membrane can have implications regarding the rejection of charged, dissolved species.

Along with hydrophobicity and charge, surface roughness, porosity, pore size, and membrane consistency can also affect the extent of fouling (Marshall 1993). The greater the surface roughness, the greater the fouling. Also, the greater the pore size, the greater the particulate fouling. Given the same operating conditions, MF membranes with large pores will foul to a greater extent than MF membranes with smaller pores.

## ***System Configuration***

Full-scale membrane elements are designed in a number of ways to optimize membrane area to element size. The types of membrane vessels include spiral wound, hollow fiber, shell in tube, and rotating disk. Spiral-wound and hollow-fiber systems provide better packing densities compared to shell-in-tube and rotating-disk units. RO and NF elements are commonly of spiral-wound configuration, whereas MF and UF are typically hollow fiber. Figure 9-12 shows a diagram of a spiral-wound vessel (Speth 1998). The membrane material is glued into envelopes with the active film to the outside. Inside the envelope, a permeate spacer sheet is added to allow for the permeate water to flow. The open edge of the envelope is attached to a permeate collection tube. Therefore, any permeate water inside the envelope will, by small pressure gradients, be transferred to the permeate collection tube. The number of envelopes attached to the permeate collection tube varies by element size and manufacturer. A feed-spacer sheet is placed in between the envelopes. The envelopes and the feed-spacer sheets are rolled into a cylinder. The permeate collection tube is plugged at one end. The other end of the permeate collection tube is



**Figure 9-12. Typical spiral-wound membrane element (Speth 1998).**

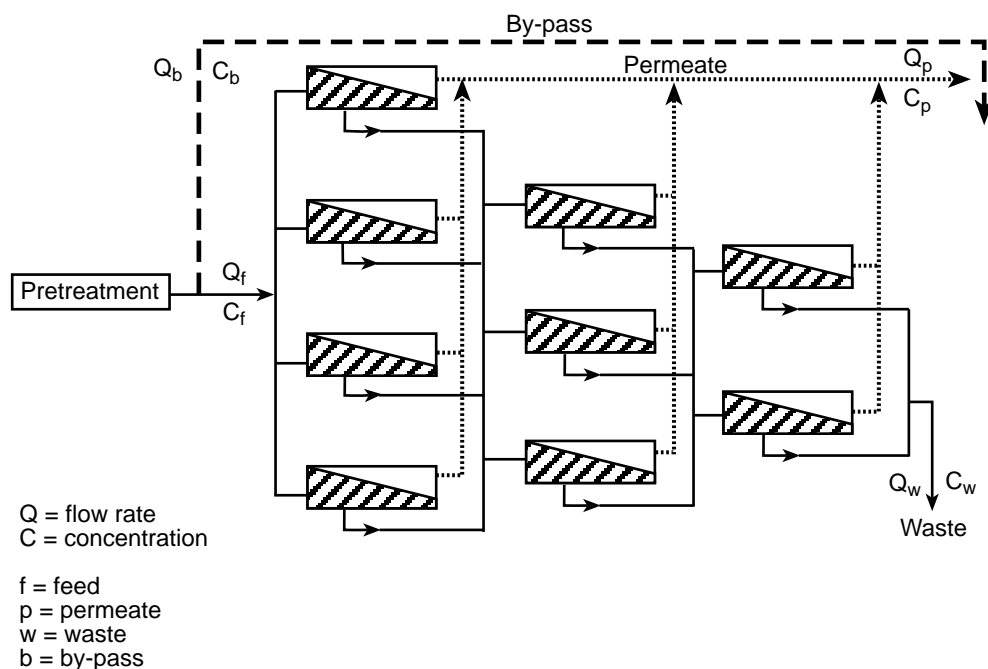
plumbed into a permeate collection line. The feed line to the element is introduced on one end of the membrane cylinder. The feed water runs through the feed-spacer sheet, past the membrane material on either side. At the end of the element, the concentrated feed water, typically referred to as the concentrate, or retentate, is plumbed into a line that is either sent to the next element in series, sent to waste, or recycled back to the feed stream.

Each NF element typically passes 10 to 15 percent of the feed water through the membrane as permeate. The remaining 85 to 90 percent of the feed water leaves the element as reject water. Percent recovery is used to give an indication of the percentage of the water that is produced.

$$\% \text{ Recovery} = (\text{permeate flow/feed flow}) \times 100 \quad (9-6)$$

Because the amount of concentrate in a single element is typically 85 percent of the feed stream flow, wasting the entire concentrate is not cost-effective. Also, in water plants, the amount of permeate water needed for consumers is large. Therefore, many elements are required to provide the requisite membrane surface area to generate the needed permeate flow. Often the membrane pressure vessels are arrayed in formations in which the concentrate of the first row of elements is fed to the second row of pressure vessels. Because of the loss of permeate water, the second and further rows of pressure vessels are fewer in number than the previous row. This maintains the cross-flow velocity across the membrane surface. Figure 9-13 shows a typical staged array (Speth 1998). Also, to save money on pressure vessels, three elements are usually placed in a single pressure vessel. For testing and research purposes, often only one element is used, with the concentrate stream being recycled to the feed stream to increase the recovery level to that associated with a staged array (typically 70 to 90 percent).

Allgeier and Summers (1995) developed a bench-scale technique using a 4x6-inch flat-plate system to predict the performance of full-scale systems. Although limited in long-term performance, researchers have shown that it can predict rejection, initial flux, and cleaning intervals for full-scale systems (Allgeier et al. 1996; Allgeier et al. 1997; Gusses et al. 1996; Speth et al. 1996; Speth et al. 1997; Gusses et al. 1999).



**Figure 9-13. Typical membrane staged array (Speth 1998).**

## **Performance**

### **Rejection**

Fronk and Lykins (1998) and Lykins and Clark (1994) showed that RO membranes rejected between 0 and 95 percent of the individual THM species. The thin-film composite membranes had superior rejection properties compared to the other membranes tested. Because precursor material is easier to reject than DBPs, NF membranes are typically only used for precursor removal.

Taylor et al. (1987) found that NF membranes rejected over 90 percent of the DOC in natural waters. Allgeier and Summers (1995) showed that for five natural waters, 67 to 94 percent of the TOC was rejected. Taylor et al. (1987) found that membranes with nominal molecular-weight cutoffs of 400 daltons or less were needed to control DBP precursors. This was confirmed by Taylor et al. (1989). Blau et al. (1992), Watson and Hornburg (1989), and Reiss et al. (1999a) also found that THM precursors could be controlled with NF. Allgeier and Summers (1995) showed that NF membranes removed THM precursors by 66 to 93 percent, haloacetic acid (HAA) six (HAA6) precursors by 67 to 97 percent, as well as precursors for other DBPs. In general, TOC rejection was a good surrogate for DBP precursor control. Speth (1998) also saw good rejection of DBP precursors for a membrane system fed conventionally treated Ohio River water (CT-ORW) for 15 months, as shown in Table 9-1.

### **Fouling and Flux Curves**

The loss of membrane efficiency due to fouling is one of the main impediments to the development of membrane processes for use in drinking water treatment. Membrane fouling is dependent on the water quality as well as the membrane's properties and construction. In general, fouling is defined as the accumulation of material on the surface, or in the pores, of a membrane that decreases the water flux through the membrane. Durham (1993) further distinguishes between membrane fouling and spacer fouling. The consequences of fouling can be severe; fouling can reduce the water flux through a membrane up to 90 percent (Belfort 1977).



**Table 9-1. Organic and Particulate Bulk Rejections for Pilot Systems Fed CT-ORW (Speth 1998)**

Parameter	Mean Feed Conc.	Bulk Rejections (%)	
		4" × 40" System	1.75" × 12" System
TOC, mg/L	1.99 (0.41,43)	94.8 (3.6,43)	95.9 (3.3,43)
UVA, 1/m	4.54 (1.39,46)	97.9 (1.2,46)	98.5 (1.4,46)
Term. THM, µg/L	224 (76,6)	95.6 (0.6,6)	96.1 (0.7,6)
SDS THM, µg/L	97 (49,6)	97.1 (1.1,6)	96.1 (4.9,6)
Term. TOX, µg/L	265 (101,6)	95.8 (0.8,6)	96.5 (1.4,6)
SDS TOX, µg/L	153 (116,6)	95.9 (3.1,6)	96.5 (4.9,6)
Turbidity, NTU	0.23 (0.08,64)	72.7 (11.8,64)	84.8 (10.9,64)
Particle counts, #/ml	882 (265,18)	99.5 (0.4,18)	99.4 (0.5,18)
HPC, CFU/µl	33.5 (27.4,25)	96.9 (4.7,25)	98.9 (3.1,25)
Aerobic spores, CFU/L	100 (NA,1)	81.8 (NA,1)	80.0 (NA,1)

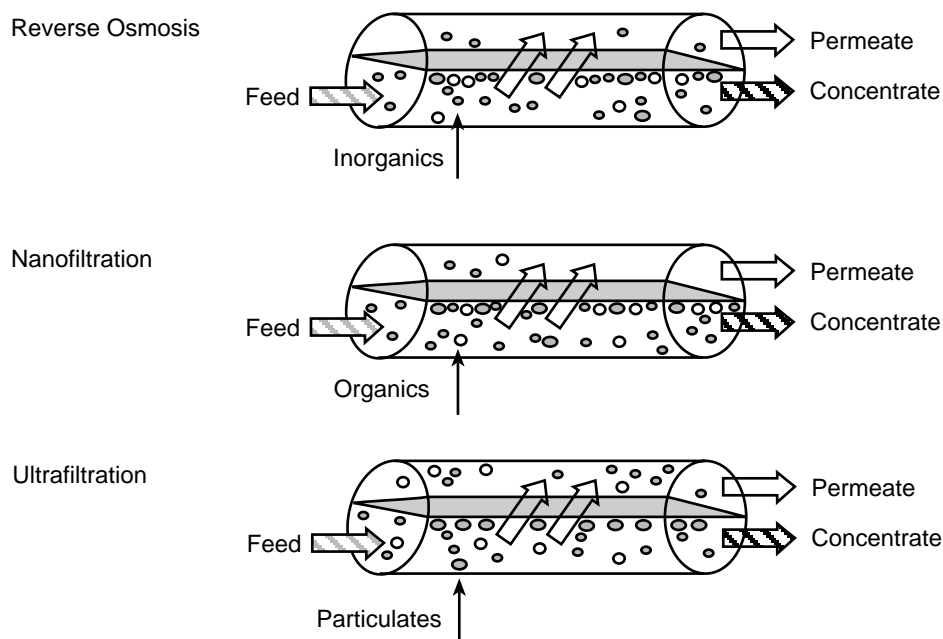
Standard deviations and number of samples are listed in parentheses, respectively.

NA = Not applicable

There are five broad fouling categories: microorganisms, colloidal or particulate matter, dissolved organics, sparingly soluble inorganics, and chemical reactants (Belfort 1977; Matthiasson and Sivik 1980; Potts et al. 1981; Barger and Carnahan 1991; Suratt 1993). Dissolved organics and colloidal matter are considered to be serious foulants due to the difficulty in removing them with pretreatment processes. Biofouling is also a serious and common fouling problem (Paul 1991). Inorganic fouling can often be controlled by acid addition. For instance, the pH needed to control calcium carbonate precipitation can be determined by a Langelier saturation index. Often, the type of foulant is operationally defined by the type of membrane cleaning agent that is effective in recovering water flux. Inorganic foulants are typically removed with acid solutions, whereas organic and biological foulants are typically removed with alkaline/detergent solutions.

Direct methods for determining the nature of the foulant include optical microscopy, scanning electron microscopy, X-ray fluorescence, atomic absorption, transmission and reflection infrared spectroscopy, energy dispersive X-ray, electron spectroscopy for chemical analysis (ESCA), pyrolysis-gas chromatograph/mass spectroscopy (GC/MS), and phospholipid analyses. Optical microscopy is useful for identifying color, size, crystalline structure, and refractive indices of foulants. Scanning electron microscopy can further refine the results determined with optical microscopy. Energy dispersive X-ray analysis and ESCA will give information regarding the elemental composition of the foulant. Infrared spectroscopy can qualitatively fingerprint the foulant in terms of functional groups and chemical structure, while pyrolysis-GC/MS can fingerprint the foulant in terms of biopolymer groupings.

For NF membranes, foulant precipitation is exacerbated by concentration polarization. Concentration polarization occurs when the convective flow of foulants toward the membrane surface is greater than the diffusional flow of foulants to the bulk solution. This only occurs before steady state is achieved. The concentration of foulants will therefore increase near the membrane until steady state is reached. Figure 9-14 shows a schematic of membrane permeation and rejection for RO, NF, and MF systems (Speth 1998). For RO and NF, the elevated concentration of foulants near the membrane surface is often the causative agent for fouling due to precipitation. In dead-end cells, where the concentrate is not removed from contact with the membrane, steady state is not achieved. The continuous accumulation of the components that are rejected by the membrane in the dead-end cells maximizes precipitation and fouling.



**Figure 9-14. Schematic of membrane permeation and rejection for RO, NF, and MF systems (Speth 1998).**

MF and UF membranes do not have the same type of concentration polarization that NF and RO membranes experience because of the lower rejection of dissolved constituents, as shown in Figure 9-14. However, UF membranes have a sparse membrane porosity that results in a local polarization phenomena that may be much greater than the average polarization (Fane and Fell 1987).

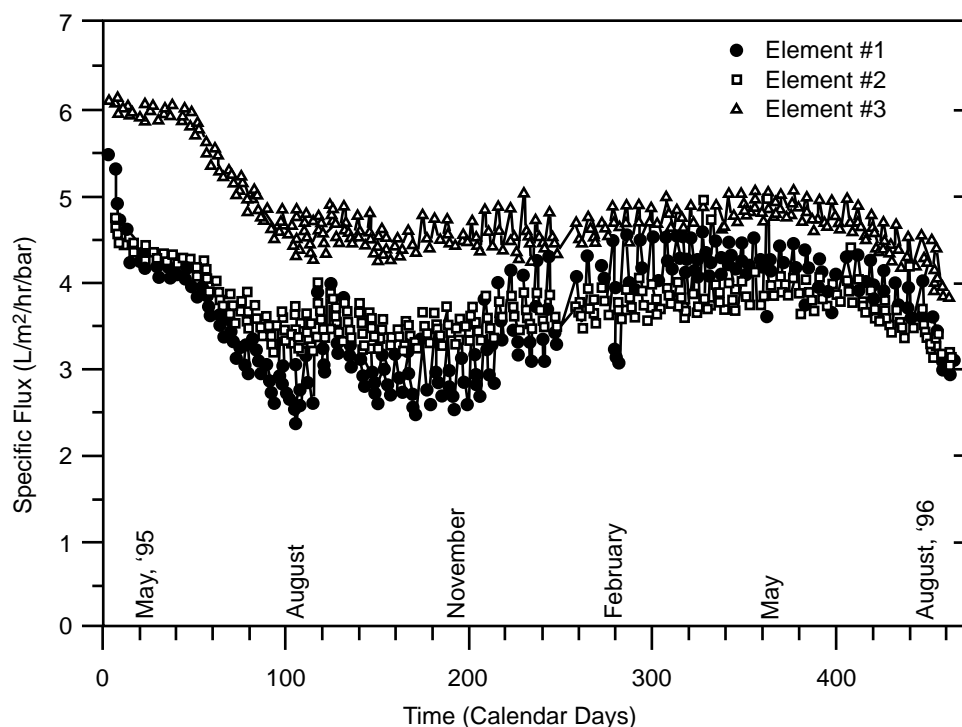
Figure 9-15 shows a flux decline curve for NF membrane elements fed CT-ORW (Speth et al. 1998). The fluxes show a distinct seasonal trend, with the greatest overall flux decline occurring in the summer and fall seasons. During these times, weekly cleaning with acid only partially offset the lost in flux due to fouling. This frequent cleaning would be difficult for a water utility to justify, but it points to the difficulty of using NF on a surface water, even a surface water such as this one with a low organic concentration (average TOC = 2.0 mg/L). Taylor et al. (1992) also have evaluated fouling from surface- and ground-water sources. They found that membranes used to treat surface waters have much higher fouling rates than membranes used to treat ground waters.

Speth et al. (1998) found that the foulant from pilot NF membrane elements fed CT-ORW was a film layer 20 to 80  $\mu\text{m}$  thick, with the greatest depth in the first of three elements in series. Heterotrophic plate counts, phospholipid analyses, and pyrolysis-GC/MS analysis of the foulant showed it to be dominated by biological growth. This explains the flux declines in the summer months.

### Flux Loss Mitigation

Improvements of fluxes can be related to flow and solution characteristics, membrane material, and pretreatment (Van den Berg and Smolders 1990). With regard to equipment design, there are many things that can be done to reduce fouling (Marshall et al. 1993). Membrane manufacturers incorporate many fouling-reducing features into their element construction.

Membranes can be fouled either by adsorption or cake-layer formation. Adsorption involves materials attaching within the pores, or matrix, of the membrane. This type of fouling is generally considered irreversible, although chemical cleaning can be effective in some cases (Belfort 1977). Cake-layer fouling, or



**Figure 9-15. Flux decline curve for NF membrane elements fed CT-ORW (Speth et al. 1998).**

reversible colmatage, involves the accumulation of material on the membrane surface. Cake-layer fouling is thought to be controlled by adjusting hydraulic operating parameters, such as cross-flow velocity or recovery of the systems. Cross-flow velocity is the velocity of the water in the feed channel, whereas recovery is the percentage of permeate flow to the total feed flow.

System recovery will dictate the concentration of dissolved species on the feed side of the membrane. The increased concentration of dissolved species on the feed side of the membrane increases the likelihood of precipitation of inorganic foulants such as calcium carbonate or barium sulfate. Organic contaminants also may be destabilized in the concentration layer. Reducing the system recovery can lead to less fouling.

The fluid pressure can also be manipulated to limit fouling. A higher pressure above the membrane will result in a greater flux of water through the membrane. Many researchers have found that the higher the initial flux, the greater the flux decline (Gutman 1977; Wilkes et al. 1996; Hong and Elimelech 1997; Chellam et al. 1998).

Changing the operating conditions can limit the amount of irreversible fouling. Crozes et al. (1997) found that increasing the cross-flow velocity, reducing the flux, and increasing the backwash frequency limited the short-term reversible fouling. This also controlled the rate of flux loss due to irreversible fouling.

As mentioned previously, the choice of membrane type will also determine the amount of fouling. Elimelech et al. (1997) and Zhu and Elimelech (1998) found that there was a significantly higher fouling rate for a thin-film composite membrane compared to that for a cellulose acetate membrane. The higher fouling rate for the thin-film composite membrane was attributed to greater surface roughness, which is inherent in interfacially polymerized aromatic polyamide composite membranes. Atomic-force microscopy and scanning-electron microscopy images supported the conclusions. The greater

surface roughness would allow for greater depositions of colloids. Ridgway and Safarik (1991) found that biofilms attached more strongly to polyamide surfaces than to cellulose acetate surfaces. They attribute the greater fouling rate of polyamide membranes to biological growth.

Along with fluid flow characteristics and membrane type, fouling can be reduced by optimizing feed-water pretreatment. This may entail adjusting the pH, adding anti-scalant agents, or using a pretreatment unit process such as coagulation, filtration, MF, and/or GAC. Typically, acid addition and anti-scalant agents are used to limit inorganic fouling. Numerous researchers have looked into pretreatment processes to reduce membrane fouling (Laine 1989; Taylor et al. 1989; Wiesner et al. 1989; Reiss and Taylor 1991; Taylor et al. 1992; Amy et al. 1993; Solomon et al. 1993; Chellam et al. 1997; Gusses et al. 1997). Processes used by these researchers were MF, coagulation/sedimentation, filtration, GAC, ozonation, and biologically active sand columns. Solomon et al. (1993) and Gusses et al. (1997) demonstrated that biological-filtration pretreatment showed the most promise with regard to reducing flux decline during UF. Chellam et al. (1997) showed that MF and UF pretreatment of a conventionally treated water gave significantly lower NF fouling rates than just conventional treatment.

For organic fouling of NF membranes, the greater the amount of hydrophobic compounds in a feed water, the greater the degree of hydrophobic adsorption, or fouling. Also, the amount of high-molecular-weight organic matter correlates to greater amounts of cake-layer formation. Carbon adsorption can be an effective, but expensive way, to control hydrophobic organic fouling.

In a follow-up study to the 15-month membrane project shown in Figure 9-15, Speth et al. (2000) evaluated five different additional pretreatments to CT-ORW. The chosen additional pretreatments were intended to produce waters with varying biological-fouling potential. Five parallel membranes were fed CT-ORW, ozonated CT-ORW, ozonated/biofiltered CT-ORW, CT-ORW reduced to 7°C, and chloraminated CT-ORW. All systems showed significant flux decline, indicating that methods beyond those needed for just biogrowth control are required for NF systems treating conventionally treated surface waters. The NF systems fed ozonated, ozonated/biofiltered, and untreated CT-ORW had the least amount of flux decline over the course of the study; however, they had significant amounts of biological growth. Fouling in these systems was attributed to the deposition of extracellular material (polysaccharides) in the cake layer, either from the biogrowth on the membrane or carryover from the pretreatment. The low-temperature system had greater flux decline, but it had lower biogrowth than the ozonated, ozonated/biofiltered, and untreated CT-ORW systems. Although lower in biogrowth, the deposited organic material in the low-temperature system still showed a strong biological signature (polysaccharides and aminosugars). The chloraminated system had the greatest flux decline, but the least amount of biogrowth. The organic material deposited in the chloraminated system showed a high level of proteinaceous character.

As mentioned previously, particulates and colloids can be major foulants. While ground waters generally do not cause concern because of the low particulates found in ground waters, surface waters require at least conventional treatment to remove particulates to acceptable levels. Typically, if the turbidity is less than one NTU, it is acceptable for membrane feed water (Potts et al. 1981).

In a comparison of conventionally pretreated surface water to riverbank-filtered water, Merkel et al. (1998) and Speth et al. (1999) found that riverbank-filtered water had significantly less flux decline than conventionally pretreated river waters. In essence, riverbank filtration changes a surface water to a ground water. Therefore, because ground waters are better source waters for NF treatment, riverbank filtration should be an effective pretreatment for a utility that wishes to utilize membrane technologies. Table 9-2 shows the percent of flux lost after 62 days for two watersheds (Speth et al. 1999). In both cases, the flux lost was much lower in the bank-filtered systems.

**Table 9-2. Flux Loss Comparison for Conventionally Treated and Riverbank-Filtration Pretreated Water (Speth et al. 1999)**

Location	Water	Length of Operation (days)	Number of Cleaning/Flux Cycles	Mean Calculated Cleaning Frequency (days)	% Flux Lost After Approx. 62 Days
Louisville Bank filtered	Ohio River	62	7	75 <sup>#</sup>	4
Louisville Conv. treated	Ohio River	79	8	36 <sup>#</sup>	46
Cincinnati Conv. treated	Ohio River	460	51	8	36
Southwestern Ohio Bank filtered	Little Miami River	79	1	62	12
Southwestern Ohio Conv. treated	Harsha Lake	70	12	8	50

Includes initial cycle.

<sup>#</sup> Not arithmetic mean, projected from slope of entire run.

### Flux Recovery Through Cleaning

There are a number of techniques that can be used to recover flux from a fouled membrane. Typically, acid cleaning is used to remove inorganic foulants. If the membrane is fouled with organic molecules (extracellular material and microbes), a detergent has been found to be successful (Ridgway et al. 1985). Hong and Elimelech (1997) found that a strong chelating agent is effective for removing free and NOM-complexed calcium ions from fouled membranes.

The type of membrane cleaner will be dependent on the membrane material. Some membranes, such as cellulose acetate membranes, are not stable over wide pH ranges. Therefore, acid/base cleaning is not practical for these membranes. Aromatic cross-linked polyamide membranes are generally incompatible with nonionic polyoxyethylene *n*-oxide detergents and cationic surfactants such as quaternary ammonium compounds. In these cases, the cleaner causes rapid and irreversible flux loss.

NF membranes are typically cleaned whenever the permeate flux decreases to 85 percent of the initial permeate flux or when the feed pressure increases to 115 percent of the initial feed pressure for elements operated at a constant flux (Fu et al. 1994). The degree of membrane fouling, which dictates the frequency of cleaning, will have a significant impact on the cost, design, and operation of full-scale facilities. Wetterau et al. (1996) showed that the efficiency of overall water production was not affected by either constant pressure or constant flux operation.

The cleaning of NF and RO membranes is completed in normal flow modes. However, backflushing the membrane has been evaluated (Breslau et al., 1980). Backflushing involves passing water from the permeate side of the membrane to the concentrate side. Backflushing has been found to increase flux, but it does not work well for removing proteins that are strongly adsorbed. Also, backflushing is not recommended for composite membranes because of the potential to destroy the thin film due to the lack of a support layer on the feed side of the membrane.

Most flux decline occurs immediately after startup or chemical cleaning. Although difficult to discern in Figure 9-15, each weekly specific flux decline curve for the membrane-fed CT-ORW was nonlinear in nature with a rapid initial specific flux decline followed by a less rapid specific flux decline. It was found

that the flux curves could be accurately fit by two linear slope segments covering the initial slope and the final slope for a typical weekly flux decline curve (Speth et al. 1998). The initial flux declines were greater than the final flux declines. The final flux declines are used to determine cleaning frequency.

### **Other Issues**

The use of coagulants and powdered adsorbents within the membrane element can improve the final water-quality of MF and UF membrane systems (Jacangelo, 1999). Coagulants and powdered adsorbents can remove DBP precursors while being rejected by the membrane. The membrane system can increase the mean residence time of the coagulant or powdered adsorbent, increasing their effectiveness. This is not an issue for RO and NF membranes because they already have excellent rejection characteristics.

### **Bromide Issues**

NF membranes reject bromide to a lesser extent than NOM or DBP precursors are rejected. Therefore, as with GAC treatment, the effluent/permeate stream will have a higher ratio of bromide to DOC than the feed stream. This will result in a greater percent of brominated DBPs than would normally occur. However, as mentioned previously, typical NF membranes reject such a high percentage of DBP precursors that the absolute amounts of brominated species reaching the consumer is very low. The bromoform to chloroform ratio is high for the membrane treated water; however, there is very little of each.

Summers et al. (1993) found that NF was effective for controlling the formation of chloroform, but it increased the relative percentage of bromo-substituted compounds to chloro-substituted ones. This was the result of higher bromide-to-organic precursor levels in the permeate water. Jacangelo et al. (1993) also found that NF reduced the amount of THMs formed, but altered the speciation of THMs and HAAs. Allgeier and Summers (1995) found that the DBPs of membrane-treated water shifted to the bromo-substituted compounds because of the preferential rejection of organic matter over bromide.

### **Blending**

As mentioned previously, blending membrane product water with pretreated membrane feed water often occurs because utilities with NF membranes wish to lower costs. Because NF can remove such a high degree of precursors, significant blending is possible, even with strict DBP limits. Not only is it more economical to blend, but it helps make the product water less corrosive (Lytle et al. 1996).

### ***Integrated Membrane Systems***

MF and UF membranes can be effective surface-water pretreatments for NF and RO membranes (Taylor et al. 1992; Robert et al. 1999; Reiss et al. 1999b). The combination of MF/UF membranes for particulate pretreatment control and NF/RO membranes for organic control is referred to as integrated membrane systems (IMS). In some hard-to-treat waters, a coagulant is needed prior to the MF/UF pretreatment (Robert et al. 1999).

The advantage of using MF or UF membranes for NF/RO pretreatment is that the MF/UF membranes will remove a sizeable percentage of pathogens. Reiss et al. (1999b) showed that IMS systems removed from 5.4 to 10.7 logs of pathogen surrogate *Bacillus subtilis*. Robert et al. (1999) showed greater than 4 logs of *Bacillus subtilis* removal. The disadvantage of using MF or UF membranes for NF/RO pretreatment is the high cost of installing two different types of membrane systems. Owen et al. (1999) found that MF removed from 4 to 6 logs of spores, while MF/NF systems together removed 8 to 11 logs of spores. Kruithof et al. (1998) found that UF membranes could remove greater than 5 logs of MS-2 phages.

## Conclusions

Activated carbon is an effective process for removing DBP precursors. It is not designed for pathogen removal. The effectiveness for precursor removal is dependent on a number of design issues such as carbon type, filter location, filter depth, filter flow rate, and blending choices. It is also dependent on a number of water quality issues such as initial precursor concentration, precursor adsorbability, precursor adsorption kinetics, temperature, dissolved oxygen levels, pH, and bromide concentration. Although much progress has been made on the modeling of GAC system performance, the applicability of this technology to any drinking water utility will need to be determined by pilot testing.

Membrane technologies are effective processes for removing DBP precursors. MF and UF membranes are excellent for removing pathogens and particulates and can be used as a replacement for conventional treatment. NF and RO membranes are excellent for removing DBP precursors, but are not counted on as a pathogen barrier due to blending and glue-line-failure issues. Reducing the effect of membrane foulants is a main consideration in the design of NF and RO plants, especially for plants treating surface waters. Although much progress has been made on modeling and scaling up small-membrane results, the applicability of this technology will need to be determined by pilot testing.

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